Experimental and Theoretical Studies of $BiVO_4$ and related materials for Photoelectrochemical Splitting of Water and Hydrogen Generation

A Synopsis for the Proposed Work for the award of degree of

Doctor of Philosophy
In Chemistry

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1. Introduction

1.1 Green Energy: Need of Present and Future Energy Requirement on Earth

World energy demand in the present times is fulfilled mainly by the fossil fuels as it accounts for 80% of the used energy. But the fossil fuel resources on the earth are limited and they are gradually depleting with the increasing energy demand. The situation is becoming more complicated because of the environmental problems associated with the use of fossil fuels in the form of CO_2 emission which at alarming level is considered to be the governing factor behind the huge global warming issue **(Styring, 2012).**

There are a variety of renewable resources available on the planet earth in the form of sunlight, wind and water. Among this sunlight has immense power that falls on earth surface in the form of radiation of 120,000 TW, hence solar energy has the potential to meet the increasing energy demands. Presently, global energy consumption is approximately 15TW which is expected to double in 2050. Use of solar energy thus becomes one of the best alternatives that can be utilized as it is available widely and in large volumes **(Chen and Jaramillo *et al*, 2010).**

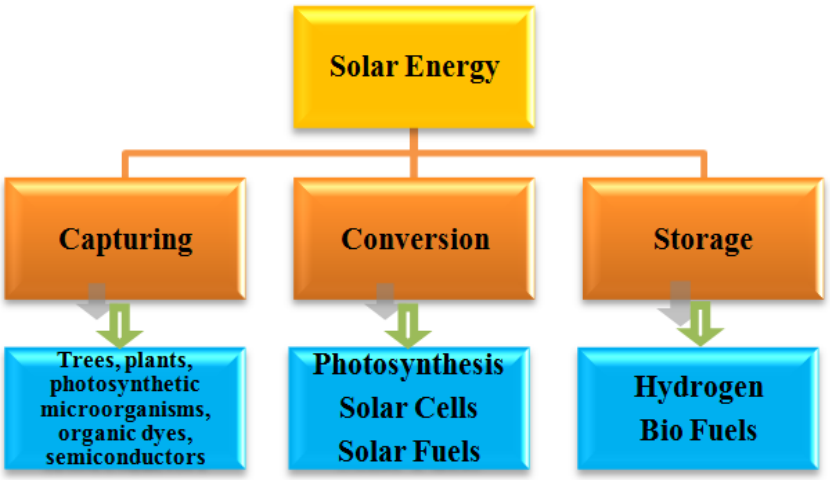


Fig.1. Scheme of utilizing sun's power, first by capturing power followed by its conversion into fuels by various mechanism and its storage in different usable form of energy (Kamat *et al*, 2010).

1.2 Hydrogen: An Environmentally Attractive Fuel

Dihydrogen is one of the simplest molecules and is present in the earth crust but not in elemental form. It is found in combination with other elements in the form of water, hydrocarbons and is also present in biomass **(Navarro *et al*, 2007)**. Globally, H_2 is playing an important role in the energy economy. In industries of petrochemicals and ammonia where production is based on H_2, globally 40 million tons of H_2 was produced (2010 data). Worldwide the demand of hydrogen as energy carrier is increasing because it can run any industry/system very smoothly as natural gas does and unlike hydrocarbons which release CO_2 on combustion, it only releases H_2O as combustion product **(Swierk and Mallouk, 2013).** Presently, the hydrogen production is based

on the raw materials mainly derived from fossil fuels (non- renewable resources) such as natural gas, heavy oil, naphtha, methanol, coal. But production dependence on other source like from biomass, wastes, nuclear, solar and wind is on a small scale **(Navarro *et al*, 2007).** For sustainable hydrogen production it should be produced from clean and recyclable sources of enegry such as solar, wind and hydraulic power. Among them, solar energy has enormous potential being clean and inexhaustible that can be used for H_2 generation. Solar energy can be utilized to generate H_2 on commercial scale, as solar energy fixes 0.1% of its energy by photosynthesis process on earth and about 0.01% of solar energy is consumed by human beings. Apart from this, solar energy has the potential to provide energy content equivalent to that present in all fossil fuels present on earth in just 7 days **(Kitano and Hara, 2010)**.

1.3 Advantages of Hydrogen as an Alternative Energy Fuel:

- ✓ Clean nonpolluting energy carrier & Inexhaustible: Because H-H bond is high energy bond and on combination with O_2, energy is released yielding H_2O as byproduct which can again be utilized as a raw material for H_2 generation **(Navarro *et al*, 2007)**.

- ✓ Efficient and Cost-effective recyclable energy carrier: Because 1 kg of H_2(high gravimetric enegry density) has equivalent energy content as 2.7 kg (1 gallon) Gasoline **(Li and Zhang, 2010).**

Based on solar energy there are broadly two ways of H_2 generation:

1. Photobiological Water Splitting
2. Photoelectrochemical Water Splitting

1.4 Artificial Photosynthesis: Photoelectrochemical (PEC) Water splitting

Photoelectrochemical (PEC) water splitting for H_2 generation is inspired by the idea of photosynthesis and is attracting attention all over the world. In this process, H_2 is produced in a single step that makes it a highly efficient process. Apart from this water is the primary reactant which is found abundantly on the earth **(Li and Zhang, 2010)**.

There are several points which make PEC water splitting a promising technology for H_2 generation **(Bak *et al*, 2002)**:

- ✓ Based on renewable sources- solar energy and water.
- ✓ Environmentally benign- no undesirable byproducts.
- ✓ Can be used on both large and small scale H_2 production.
- ✓ Integration of processes of solar light absorption and water splitting in a single photocell is possible. **(Surbhi *et al*, 2012)**

In photoelectrochemical (PEC) processes, interaction of photon (which creates electron hole pairs within a semiconductor) takes place with the electrochemical system at semiconductor/electrolyte interface.

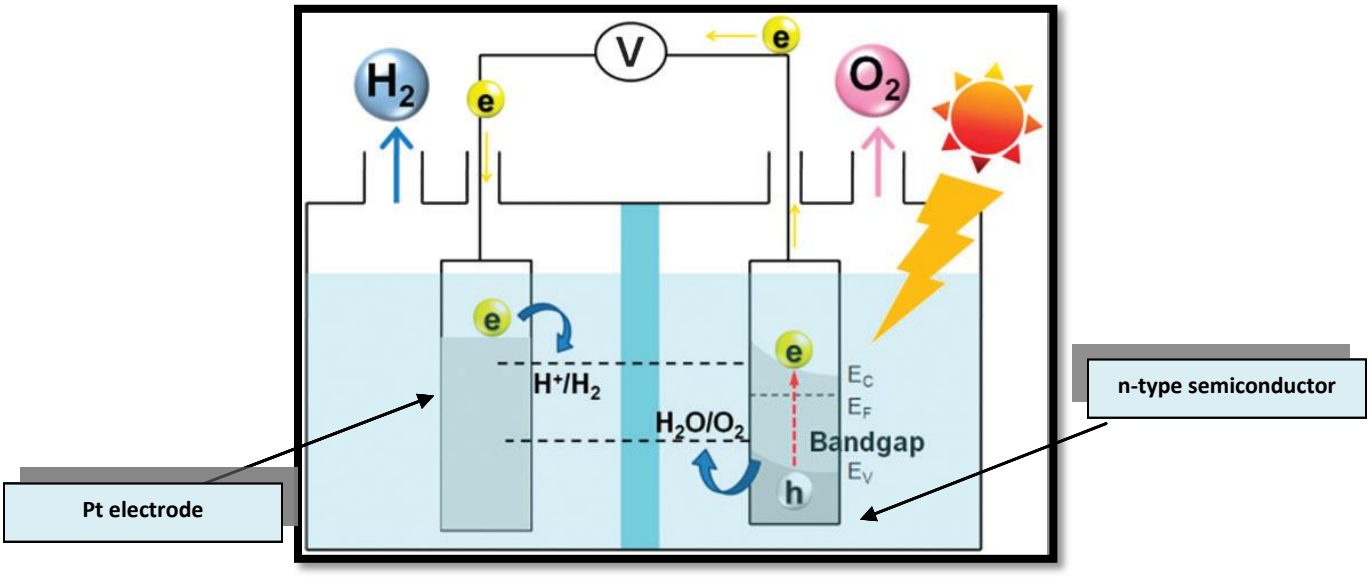


Fig.2. Photoelectrochemical water splitting with n-type semiconductor photoanode and Pt as counter electrode (Chen *et al*, 2012)

Semiconductor: Governing Factor for Photoelectrochemical Response

In a photoelectrochemical cell, when light-sensitive semiconductor photoelectrode is connected to the platinum or any other metallic electrode counter electrode with electrical wiring and are immersed in an aqueous solution and then exposed to sunlight, with energy greater than the band gap of semiconductor, electron hole pairs are generated that are spatially separated from each other due to the presence of an electric field inside the semiconductor which simultaneously interacts electrochemically at the solid/liquid interfaces with ionic species present in solution. Photoexcited holes are responsible for the oxygen-evolution reaction (OER) at the anode surface, while photoexcited electrons drive the hydrogen-evolution reaction (HER) at the cathode surface. Analogous to solid- state p-n junction, in PEC system semiconductor/liquid junction behaves as a minority carrier device allowing the flow of minority carriers only. Therefore there are two options for semiconductors:

1. *n-type semiconductors*: holes are minority carriers which are injected into the solution and O_2 is evolved, are most suited as photoanodes.
2. *p- type semiconductors*: electrons are minority carriers which are injected into the solution and H_2 is evolved, are most suited as photocathodes.

In the PEC water-splitting process, two half-reactions occur simultaneously and these are oxygen evolution reaction (OER) at the anode and hydrogen evolution reaction (HER) at the cathode and are coupled by their exchange of electrons in the solid state, and ions in solution **(Vayssieres, "On Solar Hydrogen & Nanotechnology", 2009).**

Water splitting is thermodynamically an uphill or endothermic process that requires minimum potential of 1.23V which corresponds to a Gibbs free energy change of +237 kJ/mol H_2 for the

reaction to proceed. But processes like recombination of photoexcited electron-hole pairs, and contact and electrode resistances present in the system, the optimal energy required for water splitting exceeds up to 2 eV **(Li and Zhang, 2010)**.

For an alkaline electrolyte, the reduction and oxidation reactions can be written as **(Krol, 2012)**

$4H_2O + 4e^- \rightleftharpoons 2H_2 + 4OH^-$ $\quad E^0_{red} = -0.828$ V vs. NHE

$4OH^- + 4h^+ \rightleftharpoons 2H_2O + O_2$ $\quad E^0_{ox} = -0.401$ V vs. NHE

For an acidic environment, the appropriate reactions can be written as

$4H^+ + 4e^- \rightleftharpoons 2H_2$ $\quad E^0_{red} = +0.000$ V vs. NHE

$2H_2O + 4h^+ \rightleftharpoons 4H^+ + O_2$ $\quad E^0_{ox} = -1.229$ V vs. NHE

Fundamental Conditions for Semiconductor Photoelectrode in PEC set up (Minggu *et al*, 2010):

1. PEC water splitting: $H_2O + 2\ h\nu \longrightarrow H_2 + ½\ O_2$
2. Minimum potential Required: $E^0 = 1.229$ eV
3. Optimum Potential (including losses): $E^0 = 1.6$- 2.0 eV
4. For maximum optimal absorption: UV > $h\nu$ (vis) > IR
5. Straddling Band edges of semiconductor with water redox potentials:
   Conduction Band Edge < $E^0_{H2/H+}$
   Valence Band Edge > $E^0_{O2/H2O}$

For, p-type photocathode:

Conduction band minimum (CBM) should be higher (more negative in potential) than the water reduction potential (H^+/H_2)

For, n-type photoanode:

Valence band maximum (VBM), lower (more positive in potential) than the water oxidation potential (O_2/H_2O) **(Chen *et al*, 2012)**

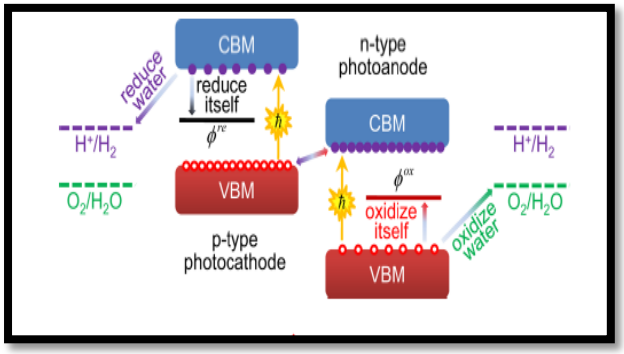


Fig.3. Band alignment of the p-type photocathode and n-type photoanode semiconductors relative to the water redox potentials (φ_{ox} oxidation potential of the photoanode in aqueous solution, and φ_{re} reduction potential of the photocathode), *Chen et al, 2012*

6. Corrosion resistance: Long-term stability in aqueous electrolyte
7. Long life time of charge carriers
8. Durability > 2000 hr
9. Low cost of manufacturing
10. Ease of maintenance

11. Conversion efficiency, solar to hydrogen (STH) > 10%

12.4% efficiency with p-/n-GaAs photoanode and a $GaInP_2$ photocathode and over 18% for a multijunction cell have been achieved, but they show performance related issues as they are not stable under operating conditions and undergo photocorrosion. Similar problems exist for most other visible light absorbing II‑VI, III‑V, and group 14 element semiconductors **(Osterloh, 2013)**.

To date, no semiconductor material satisfies all these criteria and technical requirements simultaneously and research is mainly focused in the area of developing such materials through modifications to semiconductors.

1.5 Nanostructuring of Semiconductor for Efficient PEC (Li and Zhang, 2010):

Nanostructured semiconductors offer following attractive advantages to work efficiently in PEC water splitting:

1. Large surface area for the redox reactions: Significant increase in efficiency
2. Quantum size confinement: Band gap energy and absorption coefficient increases in comparison to bulk materials due to increase in electron-hole exchange interaction.
3. Short diffusion length of photogenerated carriers: For the oxidation of water, small size of nanomaterial reduces the distance for photogenerated holes to diffuse to the photoanode/electrolyte interface.
4. Optical and electronic properties modification: By controlling nanomaterial structure, its band gap can be tuned thereby the light absorption can be increased in the solar spectrum.

Based on these advantages, solar to hydrogen conversion efficiency in the PEC can be increased many folds.

1.6 Various Modifications Adopted for Improving PEC response:

The following modifications of the materials can be used to increase photoelectrochemical response:

- Doping of wide band gap semiconductors
- Co-doping
- Dye-sensitization
- Multilayered systems and Bilayered System (coupled semiconductors)
- Surface Modification By:

  Plasmons, Quantum Dots, Etching, swift heavy ion (SHI) irradiation
- Method of preparation of nanomaterials
- Electrolyte used in PEC cell

1.7 Metal Oxides for PEC water splitting

Metal oxides can be classified mainly in two categories-
1. Large band gap semiconductors that include materials like TiO_2, WO_3, $SrTiO_3$, $BaTiO_3$, SnO_2, ZnO etc. These materials are stable in aqueous electrolyte but absorb in UV region which corresponds to only 4% of the solar spectrum.

2. Small band gap semiconductors that include materials such as Si, GaAs, InP, CdTe, CdSe, CuO etc. These materials absorb the visible portion of solar spectrum, which is of interest for photoelectrochemical water splitting, but these materials are unstable and are prone to corrosion in the aqueous systems.

Optimum band gap semiconductor includes Cu_2O which absorb in visible light but show photocorrosion. Intermediate band gap semiconductor material is Fe_2O_3 which shows absorption in the visible region but show redox level mismatch, low mobilities of holes and trapping of electrons by oxygen-deficient iron sites **(Surbhi *et al*, 2012)**.

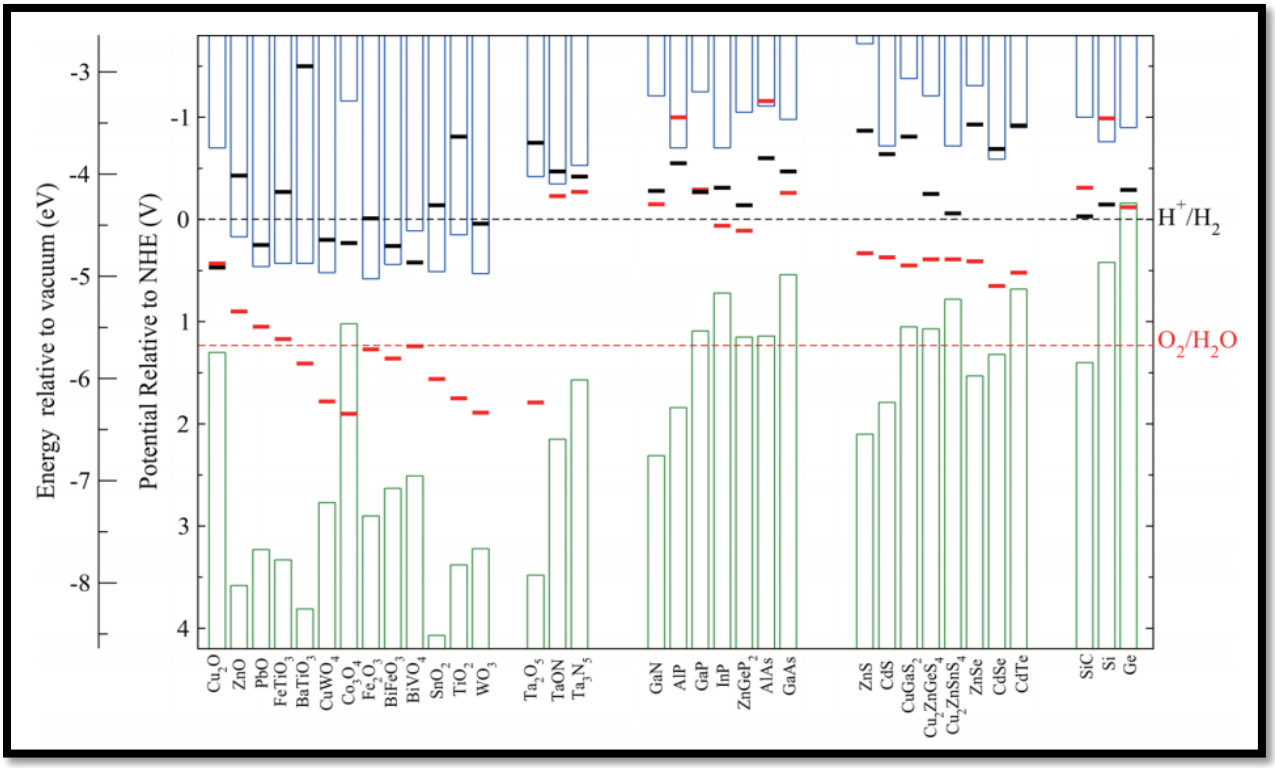


Fig.4. Band Edge positions of various semiconductors w.r.t NHE and vacuum level at at pH = 0, at temperature = 298.15 K, and pressure = 1 bar [φ_{ox} (red bars)= oxidation potential and φre (black bars)= reduction potential and valence band edge by green columns and conduction band edge by blue columns], *Chen et al, 2012*

For improving the efficiency of PEC system:

- Semiconductor material should have electrochemical stability so that the charge carriers reaching at its surface should drive only water splitting reactions without any side reactions (i.e. electrode corrosion).
- Semiconductor materials being more resistant to reduction reactions than oxidation reactions, therefore p-type material more suitable than n-type material with respect to stability.
- Stability of n-type and p-type semiconductor material can be improved by catalytic surface treatments which increase the charge transfer from semiconductor surface to the solution. **(Surbhi *et al*, 2012)**.
- *Prevention of photocorrosion in PEC system:*

  For n-type photoanode (p-type photocathode) there is a probability that photogenerated holes (photogenerated electrons) may oxidize (reduce) the semiconductor itself which is the cause of photocorrosion. Conditions of stability for photoanode and photocathode can be described as:

Photocathode (**w.r.t e^- reduction**)	Photoanode **(w.r.t h^+ oxidation**)
ϕ^{re} *(reduction potential of photocathode)* is higher than either $\phi(H^+/H_2)$ or its CBM	ϕ^{ox} *(oxidation potential of photoanode)* is lower than either $\phi(O_2/H_2O)$ or its VBM

To avoid photocorrosion in PEC system band alignment of semiconductor can be tuned (by various modifications) as well as redox potential of water (changing pH of electrolyte) so that the thermodynamic oxidation potential of n-type photoelectrode lie below the oxidation potential of water and the thermodynamic reduction potential of p-type lie above the reduction potential of water as shown in Fig. 5

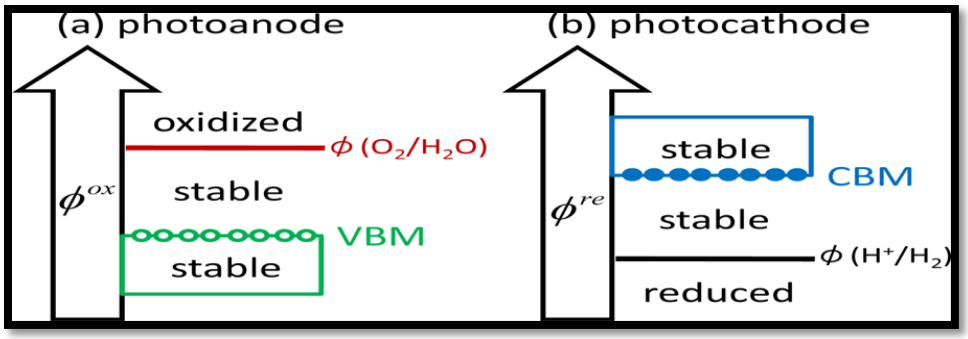


Fig.5. Stability condition of photocathode and photoanode, *Chen et al, 2012*

2. Literature Survey

Below is the summary of work done in the area of photoelectrochemical water splitting in the recent years (a decade) with different modifications emphasizing on method of preparation, characterizations and PEC response of various metal oxide materials.

- **Zhang *et al*, 2014** prepared an Al-doped ZnO inverse opal (io-AZO) structure modified $BiVO_4$ photoanode via an opal template by evaporation- induced self-assembly of polystyrene spheres (PS). Al-doped ZnO inverse opal (io-AZO) were used to facilitate the charge transport system. Scheelite monoclinic phase was obtained in XRD. Inverse opal reduces the diffusion length of charge carriers and serves as electron collector. A photocurrent of 1.5 $mAcm^{-2}$ at 1.23 V vs. RHE under AM 1.5G illumination was obtained which was three times higher than unmodified BiVO4 photoanode.

- **Ding *et al*, 2014** using DFT computations electronic structures and optical properties of $BiMO_4$ (M = V, Nb, Ta) performed to get information about their photocatalytic activities. They compared the relative ratio of effective mass and the study showed that $BiVO_4$ has superior mobility of carriers and excellent separation of photoexcited electron–hole pairs in the [010] direction due to its layered structure and the preferred distribution of electrostatic potential.

- **Qin *et al*, 2014** prepared monoclinic $BiVO_4$ film on a transparent conducting substrate for photoelectrochemical oxidation of water and films were modified further by reduction with $NaBH_4$. Photoelectrochemical performance was studied by electrochemical impedance and the Mott–Schottky. The FE-SEM images showed $BiVO_4$ crystals with diameters below 500 nm with no obvious change in morphology after reduction. Photocurrent of 2.3 mA/cm^2 was obtained under visible light due to increased donor density and effective charge carrier separation and transportation.

- **Xie *et al*, 2014** fabricated carbon dots (CDs) sensitized TiO_2. TiO_2 nanowires were grown on FTO using hydrothermal method and over it, carbon dots were decorated using pyrolysis method. To study microstructure of CDs/TiO_2, high-resolution transmission electron microscopy (HRTEM) analyses were conducted. The photoelectrochemical response of modified photoanode was five times higher than pristine TiO_2 under the visible light irradiation due to strong absorption ability of CDs under the visible light irradiation.

- **Gurudayal *et al*, 2014** prepared hematite nanorods grown on a fluorine-treated tin oxide (FTO) substrate by hydrothermal method after doping with Mn. Mott−Schottky measurement confirms the increased donor density of Mn doped alpha- Fe_2O_3 nanorods. Chronoamperometry measurements shows suppression of electron−hole recombination and enhancement in hole transport. These studies supports that 5 mol % Mn doped Fe_2O_3 nanorods shows a higher photocurrent density of 1.6 mA/cm^2 which is 75% higher than that of pristine Fe_2O_3 at 1.23 V versus RHE.

- **Sheng *et al,* 2014** fabricated quantum dot-sensitized hierarchical structure as a photoanode for photoelectrochemical water splitting. ZnO nanowires were prepared hydrothermally on Si microwires grown with the vapor-liquid-solid method. This hierarchical structure was further sensitized with CdS and CdSe quantum dots and modified with IrO_x quantum dots resulting in formation of multiple-level hierarchical heterostructure which shows remarkable light absorption and charge carrier separation. The films were characterized by FE-SEM, TEM, XRD, XPS and EDX. The system not only shows 171 times enhancement in photocurrent density compared to that from simple ZnO nanowires on a planar substrate, but also shows high stability during the water-splitting.

- **Solanki *et al,* 2013** synthesized $BaTiO_3$ films by sol-gel spin coating method. The films were irradiated with 100 MeV Si8+ ions at different ion fluences (1×10^{11}–2×10^{13} ions/cm^2). Swift heavy ion (SHI) irradiation are known to modify structural, optical and optoelectronic properties of materials after their interaction with the target atomsThe pristine and irradiated films were characterized by XRD, SEM, cross sectional SEM, AFM and UV–Vis spectrometry. Photocurrent density of 0.7 mA/cm^2 at 0.4 V/SCE was obtained for film irradiated at fluence of 5×10^{11} ions/cm^2 which was attributed to the maximum negative value of the flatband potential and donor density and lowest resistivity.

- **Luo *et al,* 2013** have done doping studies with Mo^{6+}, W^{6+} and Sn^{4+} on $BiVO_4$ system to see the photoelectrochemical water splitting performance. The pure/modified $BiVO_4$ were prepared by modified metal organic decomposition method. The films were characterized by XRD, Raman, UV-Vis transmission spectroscopy, XPS and SEM. Raman and XPS were used to reveal information about the doping site in crystal lattice of $BiVO_4$. All peaks in XRD shows the monoclinic phase of $BiVO_4$.Theoretical calculations were used to obtain formation energy of dopant ions which in turn gave the suitability of the dopant as impurity for semiconductor photoelectrodes. Poor performance of Sn-doped $BiVO_4$ is due to higher formation energy and lower solubility of impurity ions in comparison to Mo or W substituted V sites.

- **Yang *et al,* 2013** have performed theoretical calculations on visible light responsive monoclinic scheelite $BiVO_4$ which is known for its effective oxygen evolution reaction. For exploring photocatalytic water oxidation properties of different facets of $BiVO_4$ (such as (010), (110), and (011) facets), DFT calculations were used to reveal the geometric structure, optical properties, electronic structure, water adsorption, and the whole OER free-energy profiles on $BiVO_4$ (010) and (011) facets. Both favorable and unfavorable factors for OER on both facets were calculated through obtained results.

- **Liu *et al,* 2013** used global optimization evolutionary algorithm to investigate the formation of $(TiO_2)_x(Cu_2O)_y$ solid-solutions. DFT is used to get information about the electronic properties of the alloys. The study exhibited that Ti and Cu have same local environment in $(TiO_2)_x(Cu_2O)_y$ alloys as in bulk TiO_2 and Cu_2O but exception lies in some trigonal-planar Cu ions in $(TiO_2)(Cu_2O)$ alloy. The band gap of 2.1 eV was obtained which would show better performance in the absorption of visible light

compared to both binary oxides. The study proposes that the lowest formation energy of $(TiO_2)_2(Cu_2O)$ and position of its band edges makes it suitable for solar-driven water splitting applications.

- **Huang *et al,* 2013** coated silicon nanowires (SiNWs) arrays on reduced graphene oxide (rGO) by facile spin-coating method. The electrochemical impedance spectroscopy measurements suggested that the low charge transfer resistance at SiNWs-rGO interface and rGO-electrolyte interface. SiNWs/rGO composite exhibited short-circuit photocurrent density to be four times higher than that of the pristine SiNWs and more than 600 times higher than that of planar Si/rGO composite.

- **Zhang *et al,* 2012** prepared Cu_2O nanowire arrays by electrochemical anodization which were protected by carbon layer to solve photocorrosion problem. To study morphology of nanowire arrays transmission electron microscope (TEM) and scanning electron microscopy (SEM) were used. X-ray diffraction (XRD) reveals formation of crystalline Cu_2O and chemical compositions were analyzed using X-ray photoelectron spectroscopy (XPS). Photocurrent of 3.95mA/ cm^2 photocurrent was obtained at 0V vs RHE. Reduced charge transfer resistance is due to good conductivity of the carbon layer on the Cu_2O nanowire surface which facilitates the electron transfer from Cu_2O to the electrolyte.

- **Wei *et al*, 2010** have performed first-principles calculations to understand the codoping synergistic effects in metal oxide semiconductors with wide band gaps as photocatalysts. N-doped $SrTiO_3$ were used to determine the effects codopants of some nonmetal and metal codopants with sytems like N/H^-, N/X^- (X = F, Cl, Br, I), N/M^{1-} (M1 = V, Nb, Ta) and N/M^{2-} (M2 = Sc, Y, La). The study shows that the codoping of N with nonmetal atoms H, F and all metal atoms except Ta can reduce the energy cost of N doping and that further improves the solubility of N in $SrTiO_3$. Codoped structures helps in avoiding compensating vacancy defects and narrowed band gaps without recombination centers (oxygen vacancies) can be obtained. Here the exception is the N/Sc-codoped $SrTiO_3$ that shows a wider band gap than the pristine $SrTiO_3$.

- **Naseri *et al,* 2010** fabricated Au/TiO_2 Nanocomposite using Sol-gel method. XRD analysis revealed formation of anatase phase of TiO_2 along with Au nanocrystals peak. Optical density spectra further confirms the formation of gold nanoparticles. Bandgap energy of the Au: TiO_2 films decreased with increasing Au concentration. Au NPs (5 mol%) showed two times higher photoresponse than the plain TiO_2 at increased annealing temperature.

- **Huda *et al,* 2008** have applied local density approximation to density-functional theory for effect of impurities in monoclinic WO_3 at room-temperature to get understanding about the suitable candidates for water splitting for H_2 generation. They studied the effect of nitrogen impurity in WO_3 in both substitutional and interstitial cases. They found that band gap reduction is due to the formation of impurity bands in the band gap. The electronic properties of the foreign atom and their concentration changes of band-edge positions, valence-band maxima and conduction-band minima.

- **Tokunaga *et al*, 2001** have studied photocatalytic activity of $BiVO_4$ which is a ferroelastic and ion conductive material and crystal form rules its properties .The three main crystal forms of $BiVO_4$ are
  1. Zircon structure with tetragonal system (z-t)
  2. Scheelite structure with monoclinic (s-m) system
  3. Scheelite structure with tetragonal (s-t) system

  Under visible light irradiation, the photocatalytic activity of monoclinic $BiVO_4$ is found to be higher due to presence of a $6s^2$ lone pair of Bi^{3+} which causes distortion of a Bi-O polyhedron.

2.1 $BiVO_4$ as a promising material for PEC cell

Monoclinic bismuth vanadate ($BiVO_4$) has been considered a promising material for photoelectrochemical water oxidation due to

(i) its moderate bandgap (2.4 eV)

(ii) appropriate band edge positions

These properties allow it to absorb as much as 11% of the solar spectrum to drive the water splitting reactions. Assuming a quantum yield of 100% in $BiVO_4$, photocurrents of 7.5 mA cm^{-2} could be achieved under AM 1.5G illumination.

The drawbacks associated with the use of semiconductor include:

(i) Charge carriers with low mobility

(ii) Slow kinetics of water oxidation

(iii) High recombination rates of electron–hole **(He *et al*, 2014)**.

2.2 Theoretical Study Using Density Functional Theory (DFT):

To investigate the electronic structure of many-body systems principally in their ground state (particularly atoms, molecules, and the condensed phases), ***density functional theory (DFT)*** is used which is a computational quantum mechanical modelling method used in physics, chemistry and materials science. The theory uses the properties of a many-electron system which can be determined by using functionals, i.e. functions of another function, which is the spatially dependent electron density. The name therefore, density functional theory comes from the use of functionals of the electron density. DFT is one of the most popular and versatile method available in condensed matter physics, computational physics and computational chemistry. **(http://en.wikipedia.org/wiki/Density_functional_theory)**

Theoretical studies can be performed in order to get better understanding of electronic and structural properties including bulk and surface characteristics which could be used to meet technical challenges in the development of new materials for their use in PEC technology for hydrogen production. These calculations are helpful in saving time, chemicals and guides to develop an efficient material.

Theoretical modeling of PEC water splitting can be done by studying the bulk, surface and interface properties of semiconductor materials.

(i) Bulk properties study includes band engineering for tuning band gap, band edges, optical properties and carrier mobility etc.

(ii) Surface properties study includes basic understanding of molecular absorption/dissociation on the surface, simple catalytic activity, surface doping etc.

(iii) Interface properties (semiconductor/electrolyte) study includes reaction mechanism, reaction energetic, material stability in solution, etc.
(http://www.hydrogen.energy.gov/pdfs/review12/pd052_huda_2012_p.pdf).

The present study therefore is aimed at performing surface calculations, i.e. calculation of band edge positions of different metal oxides with respect to vaccum level and water redox potential using DFT calculations which is to the best of our knowledge has not been performed so far with respect to PEC system and validating the same experimentally by preparing thin films and pellets and then performing PEC studies with the following objectives as stated below.

3. Objectives of Study

The tentative plan of proposed work includes following objectives:

1. **Preparation of nanostructured metal oxides ($BiVO_4$, Fe_2O_3, Cu_2O)**:
   The nanostructured thin films will be prepared by sol-gel, spray pyrolysis and electrodeposition method.
   Pellets would be prepared by sol-gel method.

2. **Modification:** *Atomic percent doping* with various ions (W, Mo, N, Nb etc) at their different concentration.

3. **Theoretical Calculations:**
   The cluster present in the department of Chemistry will be used for calculations with the QUANTUM ESPRESSO software package which is based on the density functional theory using the plane-wave pseudopotential (PWP) formalism, employing ultra-soft and norm-conserve pesudopotentials. The generalized gradient approximation (GGA) pseudopotentials of Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional would be employed. Main focus will be on the structural and electronic properties of semiconductors determining the band edge positions with respect to vaccum level and its compatibility with redox level of water for the exchange of charge carriers.

4. **Characterization of Prepared Nanomaterials:**

   a. XRD:

Formation of different phases and crystallinity of the sample will be confirmed by XRD and Scherrer's equation will be used to estimate the average grain/particle size.

b. SEM and AFM:

Surface morphology, topography for the prepared grain structure and roughness of the films will be studied using scanning electron microscope (SEM) and atomic force microscope (AFM) analysis.

c. Band-gap (UV- Visible Spectroscopy):

Tauc plots will be used to determine the band gap, E_g by plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$ using the equation below:

$$\text{Absorption coefficient, } \alpha = A\,(h\nu - E_g)^{1/2}$$

d. Film Thickness:

Thickness of thin films would be measured by surface profilometer available with the research group at D.E.I.

e. Mott-Schottky plot:

To measure capacitance (C) at semiconductor electrolyte junction, LCR meter will be used. Plot between $1/C^2$ versus electrode voltage plot will give band bending, flatband potential and donor/acceptor densities with the help of following Mott-Schottky equation.

$$\frac{1}{C^2} = \left(\frac{2}{q\varepsilon_o \varepsilon N_D}\right)\left(V_{app} - V_{FB} - \frac{kT}{q}\right)$$

Where ε_o is the permittivity of the vacuum, N_D is the donor density, V_{app} is the applied potential, ε is the dielectric constant of the semiconductor, kT/q is the temperature dependent term.

Nature of semiconductor will be determined by the slope of the graph obtained:

+ve Slope- n- type

-ve Slope- p- type

5. Photoelectrochemical Studies

Photoelectrochemical behavior of thin films and pellets of nanostructured metal oxides will be studied both in dark and under illumination condition at different electrolytic conditions (pH, nature of electrolyte etc.) in order to optimize the conditions of H_2 evolution in conjunction with platinum counter electrode and saturated calomel electrode (SCE, as reference electrode). 300W Solar Simulated light source will employed for this purpose. I-V characteristics of the semiconductor will be studied and onset voltage for photocurrent would be determined, and based on these measurements the PEC performance would be evaluated.

Evolved H_2 gases from PEC cell will then be analysed for its purity and for that it will be passed through alkaline pyrogallol solution at 0-5°C to remove oxygen. Rest of the gas (largely hydrogen) will then be collected in a gas measuring tube, slowly, by displacing the water. The

collected gas would be analyzed for hydrogen by employing a gas chromatograph and efficiency of hydrogen production would be calculated.

4. Pilot Study (First-principles Calculations)

Surface calculations for band edge alignment with respect to vaccum level and DOS (density of states) of different layered structure of $BiVO_4$ is calculated using DFT. The theoretical study was confirmed with the experimental results of other investigators who have reported results on $BiVO_4$ **(Zhao *et al*, 2011)**.

4.1 Computational details:

Density functional theory with plane wave pseudopotential was used. The calculations were performed with Quantum espresso package with the generalized gradient approximation (GGA) pseudopotentials of Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional. The energy cut-off was chosen as 50 Ry for all calculations and that for charge density and kinetic energy 400 Ry for bulk structure optimization and 300 Ry for surface calculations. The integration over the Brillouin zone was performed on a Monkhorst-pack grid of 6×4×8 for bulk structure optimization and 3×1×4 for surface calculations.

4.2 Structure:

The calculated and experimental lattice constants of $BiVO_4$ crystal are listed in Table 1 given below. The calculated lattice constants are very close to experimental results **(Zhao *et al*, 2011)** and lie within the DFT accuracy of less than 1%.
The conventional cell of monoclinic clinobisvanite $BiVO_4$ structure considered in the present work is displayed in Fig. 6. Space group is *C2/c*, and point group is C^6_{2h}. The structure contains four bismuth, four vanadium and sixteen oxygen atoms in a unit cell.

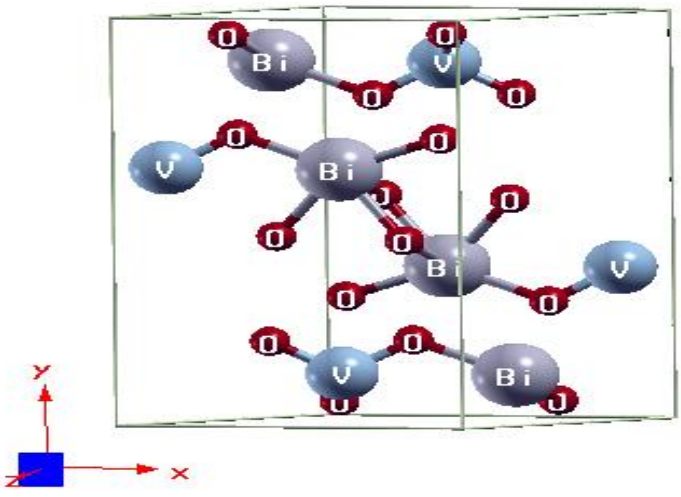


Fig. 6. The crystal structure of monoclinic clinobisvanite $BiVO_4$

	a(Å)	b(Å)	c(Å)	α	β	ϒ
This work	7.214	11.524	5.102	90	134.99	90
Experimental (Zhao *et al*)	7.247	11.697	5.090	90	134.226	90
DFT (Zhao *et al*)	7.224	11.522	5.108	90	135.003	90

Table 1. Optimized crystallographic parameters of monoclinic $BiVO_4$

Total DOS and partial DOS of bulk $BiVO_4$ are plotted in Fig. 7. Red, blue, green and black curves represent Bi, O, V and total DOS, respectively. The valence band is mainly composed of states of O whereas conduction band mainly composed of states of V. The band gap obtained by the DOS plot is 1.98 eV whereas the experimental band gap of $BiVO_4$ is 2.4 eV.

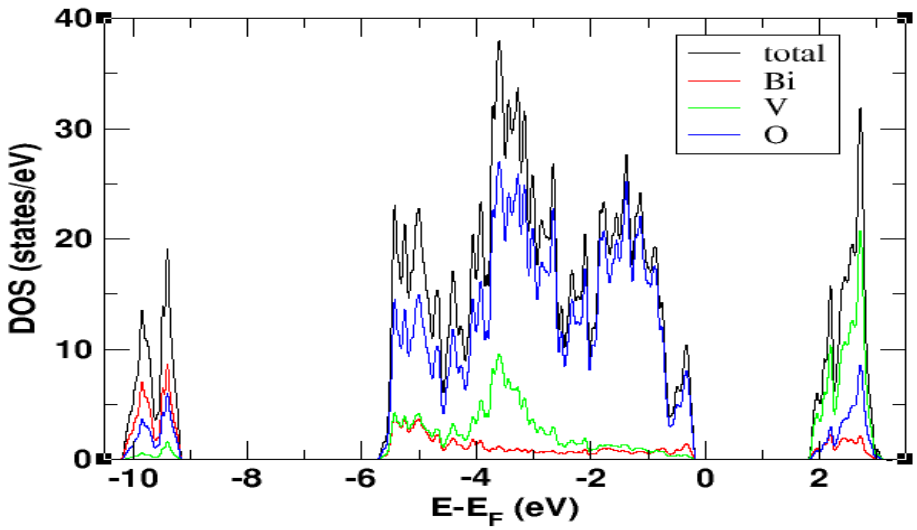


Fig. 7. Density of States (DOS) of $BiVO_4$

4.3 Surface Calculations

Calculations are performed for different layered structures of $BiVO_4$ for 10 and 12 A vaccum in y-direction.

Different layered structures of $BiVO_4$ were considered from the bulk $BiVO_4$ with 10A, 12A vaccum in y-direction. We named the structures L1, L2, L3 shown in Fig. 8.

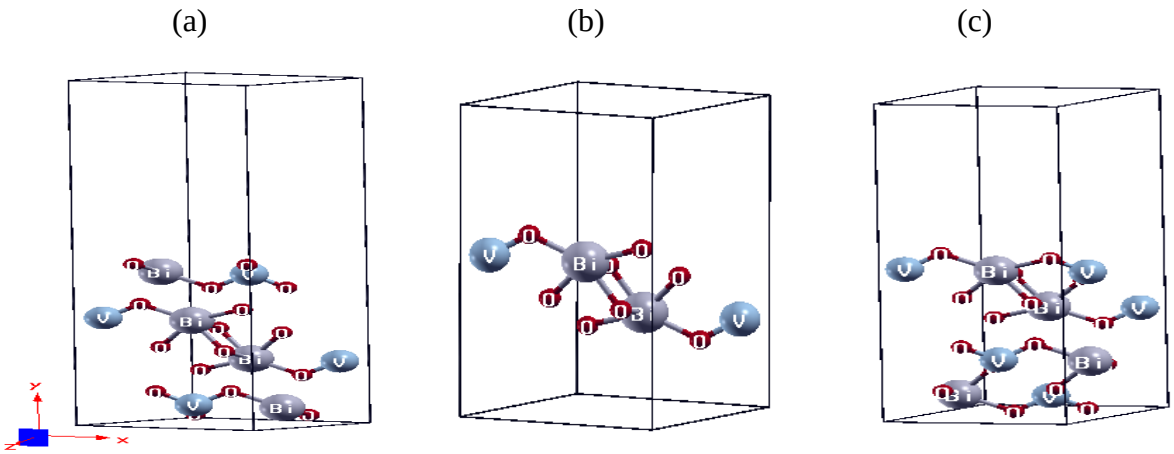


Fig. 8. Three layered structure with 24 atoms and 12A vaccum (a), 1 layered structure with 12 atoms and 10A vaccum (b), 2 layered structure with 24 atoms and 10A vaccum (c).

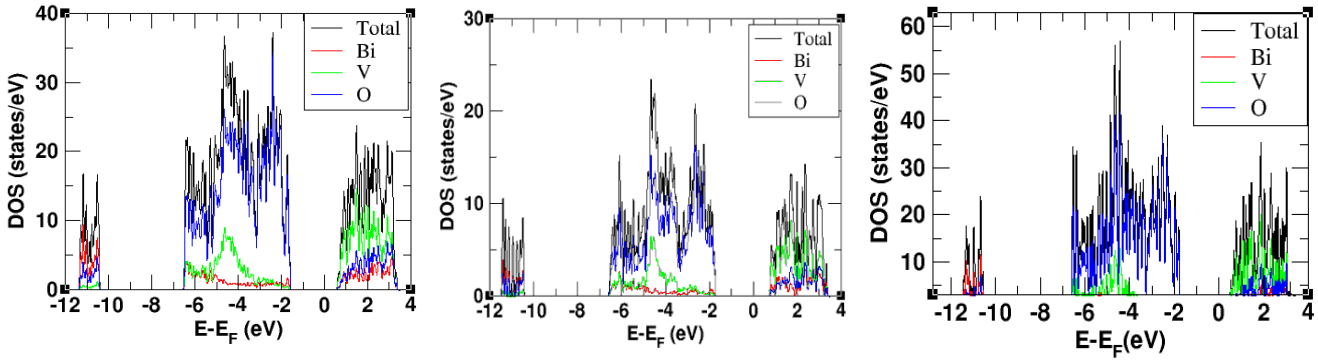
4.4 Density of states (DOS) of different layered structures

Obtained band gap of L1, L2, L3 are 2.09, 2.43, 2.10 eV respectively and the band edge positions do not vary much with varying layered structures.

The band edge positions observed in DOS plots of different layered structure and the bulk given in the table below.

Structure	Surface energy (J/m^2)	Band Gap (eV)
L1	0.2096	2.09
L2	0.232	2.43
L3	0.2598	2.10
Bulk	-	1.98

Table.2 Band edge positions in DOS of different layered structure L1, L2, L3 and the bulk



(a) (b) (c)

Fig. 9. Density of States (DOS) of L1 (a), L2 (b) and L3(c)

4.5 Band alignment study of different layered structures of $BiVO_4$

Vaccum level position of different layered structures was calculated and the band alignment with respect to the vaccum level was found. According to the calculation, the band edge alignment is such that, it will favour the oxygen evolution reaction at the $BiVO_4$ electrode in photoelectrochemical splitting of water because valence band maxima lies below the OER potential and it is energetically favourable condition for the holes to be transferred to the electrolyte for participating in OER. Band alignment condition for the OER is maintained in all the three layered structures which can be seen in Fig 9.

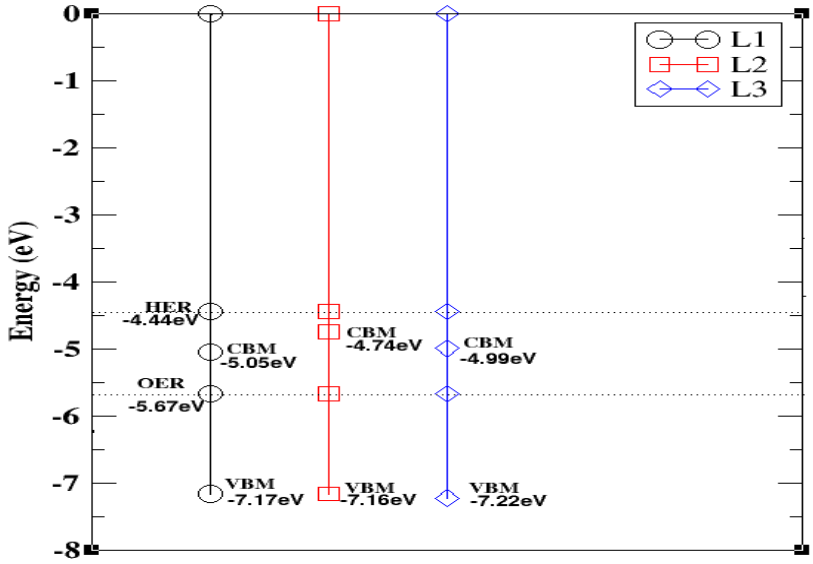


Fig. 9. Band edge alignment with respect to vaccum level for L1, L2, L3.

4.6 Conclusions

We reported First-principles calculations result performed to investigate the structure and band alignment of $BiVO_4$. The calculated structures agrees well with the experimental and theoretical results **(Zhao *et al*, 2011)**. It is observed that $BiVO_4$ can be used as a photoanode in photoelectrochemical splitting of water since its valence band lies 1.50 to 1.55 eV below the water redox potential.

5. Expected Outcome

Based on DFT calculations for band edge positions of the semiconductor under study with respect to water redox potential selection of most suited material can be easily predicted for carrying out studies related to photoelectrochemical water splitting. Such studies would not only allow one to focus on material with desired properties but would also save on hit and trial experimentation, valuable consumables, energy and time.

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